E-20-J47
#1

Potential for Alkali-Silica Reaction in Hollow Glass Spheres to be used in Oil Well Cementing Applications

Prepared by:
Krissy Thibodeaux
Luke Kennison
Kimberly Kurtis

School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0355

Submitted to:
Manny J. Arco
3M Corporation
3M Center
Bldg 236-2A-01
Maplewood, MN 55144

September 15, 2003

Executive Summary

This research addresses the potential for alkali-silica reaction from hollow glass spheres to be used in oil well cementing applications. Alkali-silica reaction (ASR) occurs in cement-based materials between the strongly alkaline pore solution and reactive silica(tes) which may be present in the aggregate. The product is a gel that, in the presence of a sufficient amount of moisture, swells. The swelling gel may lead to expansion and microcracking of the matrix and aggregate. In mixtures containing hollow glass spheres, the glass provides the source of reactive silica. It is important, then, to assess if the presence of this aggregate may lead to expansion by ASR.

ASTM C 227 was used to gauge the reactivity of the hollow glass spheres. In this test, initial length measurements are taken after demolding the mortar bars. The bars are stored upright in a tank at 38°C and 100% humidity – conditions meant to accelerate the reaction. Subsequent length measurements were taken at 14, 28, 56, 85, 113, and 172 days. Aggregate is deemed reactive if expansion exceeds 0.05% at 3 months (85 days) or 0.10% at 6 months (172 days). Mortar bars were cast with varying cement types, water-to-cement ratios, and equivalent alkali contents to both meet ASTM C 227 requirements as closely as possible and to simulate field conditions. Five mixes were developed, and two batches were cast per mix. In addition, flexure testing was performed to monitor any loss in strength due to microcracking from ASR. Mortar bars for flexure testing were stored in a limewater bath. Additional mortar bars were cured both under ASTM C 227 conditions and in the limewater bath to assess the effect of curing type on flexural strength. Fracture surfaces of mortar bars broken in flexure were examined by stereo optical microscopy and confocal microscopy.

ASTM C227 results show a net shrinkage in mortar bars cast from all mixes, rather than expansion. Shrinkage is believed to be attributed to autogenous and/or carbonation shrinkage. Autogenous shrinkage is likely due to the high porosity and low stiffness of the HGS. Some batches experienced expansion after an initial period of shrinkage; however, the net length change was negative at all testing times for all mortar bars. Also, trends in length change appear to have stabilized, for most specimens, between 113 and 172 days. Large standard deviations were encountered; it was noticed that different batches produced from the same mix design may produce varying results. Flexural strength generally increased with time, indicating no loss of flexural strength from ASR over the period examined. Mortar bars cured under the different curing conditions showed conflicting results. Generally, mortar bars cured by the ASTM C 227 conditions showed increased flexural strength as compared to those cured in the limewater bath. This observed trend was not expected, as ASTM C 227 curing conditions are believed to increase the potential for ASR, thus introducing more microcracking. While microscopy did not reveal any microcracking, features were apparent around the aggregate that could indicate the presence of reaction gel or aggregate/paste debonding. This observance was limited, however. Continued monitoring of samples at later exposure times by microscopy is recommended.

Continued testing is suggested to gauge the reactivity of the HGS before their use in oil well cementing. ASTM C 227 can be unconservative and ASTM C 1260 has previously shown this aggregate to be reactive. Therefore testing with ASTM C 1293 is suggested. Due to the large standard deviations seen with flexure testing, splitting tensile strength or compressive strength may also be considered as mechanical tests to accompany expansion measurements.

In addition, measurements of autogenous shrinkage are recommended.

Table of Contents

1.0 Introduction	1
2.0 Experimental Procedure	2
2.1 Rationale for Selection of Test Methods	2
2.2 Mix Design	2
2.3 Modifications to ASTM C 227	3
2.4 Aggregate Content	3
2.5 Aggregate Gradation	4
2.6 Alkali Content	4
2.7 Water-to-Cement Ratio	4
2.8 Mixing and Casting Mortar Bars	5
2.9 Expansion Test	5
2.10 Flexure Test	6
2.11 Microscopy	6
3.0 Results and Discussion	7
3.1 Length Change	7
3.1.1 Results	7
3.1.2 Discussion	11
3.2 Flexural Strength	14
3.2.1 Results	14
3.2.2 Discussion	16
3.3 Microscopy	17
4.0 Conclusion and Recommendations	20

List of Tables

Table 1: Mix Proportions 3
Table 2: Gradation Requirement for ASTM C 227 4
Table 3: Average Free Shrinkage and Standard Deviation 8
Table 4: Standard Deviation of Modulus of Rupture Data, Mixes f1-5, Limewater Bath 14
Table 5: Standard Deviations of Modulus of Rupture Data, Mixes 1and 2, Limewater Bath and ASR Tank 15

List of Figures

Figure 1: Free Shrinkage vs. Time of Mortar Bars 7
Figure 2 (a): Expansion of Individual Mortar Bars, Mix 1 8
(b): Expansion of Individual Mortar Bars, Mix 2 9
(c): Expansion of Individual Mortar Bars, Mix 3 9
(d): Expansion of Individual Mortar Bars, Mix 1 10
(e): Expansion of Individual Mortar Bars, Mix 1 10
Figure 3: Modulus of Rupture for Mortar Bars Cured in Limewater Bath 14
Figure 4: Comparison of Modulus of Rupture for Limewater Bath Curing and ASR Tank Curing up to 14 days of Exposure 15
Figure 5: Comparison of Modulus of Rupture for Limewater Bath Curing and ASR Tank Curing at 83 days of age 15
Figure 6 (a): Mix 1, 14 days, ASR tank, Confocal Microscope 17
(b): Mix 1, 14 days, ASR tank, Stereo Microscope 17
(c): Mix 2, 14 days, ASR tank, Confocal Microscope 17
(d): Mix 2, 14 days, ASR tank, Stereo Microscope 17
(e): Mix 1, 85 days, Limewater Bath, Confocal Microscope 18
(f): Mix 1, 85 days, Limewater Bath, Stereo Microscope 18
(g): Mix 2, 85 days, Limewater Bath, Confocal Microscope 18
(h): Mix 2, 85 days, Limewater Bath, Stereo Microscope 18
(i): Mix 6, 83 days, ASR tank, Confocal Microscope 19
(j): Mix 6, 83 days, ASR tank, Stereo Microscope 19
(k): Mix 7, 83 days, ASR tank, Confocal Microscope 19
(l): 83 days, ASR Mix 7,tank, Stereo Microscope 19

1.0 Introduction

Alkali-silica reaction in concrete or mortar occurs from the reaction of the strongly alkaline pore solution with reactive siliceous aggregate. Concrete is composed of aggregate, solid hydration products, residual unhydrated cement, air, and pore solution. The pore solution consists largely of sodium, potassium, hydroxyl, and calcium ions, among others. A siliceous aggregate's surface contains incomplete silica tetrahedra that are first attacked by the hydroxyl ions in the pore solution, followed by the alkalis. The product of this reaction is a gel that expands in the presence of a sufficient amount water. Thus, damage from this reaction will occur only when the three necessary components - reactive silica or silicates, alkalis, and moisture – are present in sufficient concentrations or amounts.

The reactivity of aggregate for alkali-silica reaction is dictated by many factors including mineralogy, particle size, density, and equivalent alkali content of the mortar or concrete. The amorphous structure of glass makes this material especially susceptible to the reaction. In addition, the small particle size of the HGS increases the surface area available for reaction, and thus potentially increases the reactivity. Increasing expansion due to ASR with decreasing particle size is believed to occur only to a pessimum size value at which maximum expansion occurs; particle sizes below the pessimum have decreasing expansion with decreasing particle size. A pessimum size for glass was found to be between 1.18-2.36 mm by Jin, Meyer, and Baxter (2000) and 75 μm by Hudec and Ghamari (2000). Low density aggregate has been found to decrease expansion from ASR (Ducman et al 2002 and Boyd et al 2000). The reduced expansion is due primarily to the ingress of the reaction product gel into the porous aggregate, thus not inducing stress and expansion on the surrounding cement paste. For the HGS, expansion reduction through these means would occur only if the entire particle was consumed in the reaction, since the particle walls are unlikely to be permeable to the reaction product gel.

The high temperature and high pressure conditions present during oil well cementing applications may exacerbate this reaction as well. Several researchers have shown the effects of elevated temperatures and pressures on ASR by use of autoclave testing. Tang et al (1983) and Fournier and Berube (1991) showed increasing expansion with increasing temperature and pressure using an autoclave method of ASR testing. No standard test for ASR using this method has been established.

Alkali-silica reaction can cause substantial problems in concrete or mortar, including expansion and microcracking. As a result, strength (particularly in flexure and tension) and stiffness are decreased. In addition, permeability may be increased, decreasing the materials resistance to freeze/thaw damage, chloride ingress, sulfate attack, and other durability issues. In oil well cementing, the hardened cement slurry is used for zonal isolation to prevent gas, oil, water, and other fluids from penetrating other zones (Smith 1990). Microcracking of the hardened slurry could disrupt this zonal isolation. Thus, the reactivity of the HGS must be determined before their use in oil well cementing applications.

2.0 Experimental Procedure

2.1 Rationale for Selection of Test Methods

The expansion of mortar bars cast with HGS will be used to assess the potential of the aggregate for alkali-silica reaction. ASTM C 227 was chosen to gauge the potential for expansion from alkali-silica reaction of the HGS. ASTM C 1260 has previously shown this aggregate to be reactive, resulting in an expansion of 0.893% after 13 days (Arco 2002). Since ASTM C 1260 can be overly conservative, additional testing is suggested before the aggregate is labeled deleterious. The ASTM C 227 test was chosen over ASTM C 1293 for several reasons. ASTM C 1293 is designed for concrete, thus the gradation requires the use of coarse aggregate. Since oil well applications utilize slurries containing fine materials rather than concrete, the mix requirements for ASTM C 227 more closely resemble the intended field use. In addition, w/c required by ASTM C 1293 is between 0.42 and 0.45. Given the extreme fineness of the HGS, using a w/c in this range would produce a mortar that was unworkable. In addition, the use of admixtures in not allowed in ASTM C 1293; therefore superplasticizer could not be added to increase the workability. In contrast, ASTM C 227 requires a mortar flow between 105%-120%, allowing the w/c to be adjusted as necessary, and the use of admixtures is not prohibited. The autoclaving test method for alkali-silica reactivity utilizes high temperatures and pressures to accelerate and exacerbate the reaction. An ASTM standard for use of this method to test ASR does not exist. Although the high temperatures and pressures used in autoclaving are relevant to oil well applications, no limits on expansion have been set. Further, this test is not specifically designed for alkali-reactivity assessment.

In addition to expansion measurements, flexure tests are performed to monitor the strength of the mortar bars as a function of time to determine any strength loss due to alkali-silica reaction. Flexural behavior of mortar is likely to be sensitive to cracking, which typically accompanies ASR. Ahmed, Burley, and Rigden (1999) found significant differences in both flexural strength and compressive strength from mortar bars with reactive and non-reactive aggregate. Monette, Gardner, and Grattan-Bellew (2002) found that flexure strength, but not compressive strength, of reinforced concrete bars was affected by ASR. Flexural test were included in this study to provide complementary data to the expansion measurements. There is no set limit on strength gain or loss to indicate whether an aggregate is reactive or innocuous.

2.2 Mix Design

Seven mix designs were developed with variations in cement type, alkali content, and w/c. Table 1 gives the mix parameters used in this study in proportion by weight. Mixes 1-5 are tested for expansion and flexure. Mortar bars for flexure test are cured in limewater bath (i.e., standard curing); Mixes 1, 2, 6, and 7 are tested in flexure and are cured under ASTM C 227 conditions or in the limewater bath.

Table 1: Mix proportions

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7
cement type	H	A	H	A	H	H	A
NaOe (cement) (%)	0.325	0.479	0.325	0.479	0.325	0.325	0.479
cement	1	1	1	1	1	1	1
HGS	0.414	0.414	0.414	0.414	0.414	0.414	0.414
water	0.75	0.75	0.75	0.75	1	0.84	0.81
NaOe (%)	1	1	0.325	0.479	1	0.325	0.479

The mixes consisted of 900 g of cement with materials proportioned as above. The equivalent alkali content for Mixes 1, 2, and 5 were increased by adding sodium hydroxide (NaOH) to the mix water. Superplasticizer was added to the mix as needed to obtain the desired flow. For mixes with Class H cement, the amount of superplasticizer was approximately 4.2 μL of superplasticizer per gram of cement, and approximately 2.2 μL of superplasticizer per gram of cement for Class A cement. The increased amount of superplasticizer in the Type H cement is due to its apparent increased fineness, which in turn decreases workability. From API 10A Class A cement has a minimum SSA of 150 kg/m^3. Class H cement does not have a fineness requirement, but typical values range from 220-300 kg/m^3 (Bensted 1992).

Mixes 1 and 2 meet ASTM C 227 standards for flow and alkali content using Class H and Class A cement, respectively; therefore these mixes are considered the control mixes. Expansion results from Mixes 1 and 2 will govern in terms of labeling the HGS as innocuous or deleterious. Mixes 3 and 4 meet flow but not alkali content requirements, and are included in the study to assess expansion in actual field mix designs. Similarly, Mix 5 meets alkali content requirements, but w/c is not chosen based on flow requirements of ASTM C 227. This w/c did, however, produce a slurry with a flow within the specified range.

2.3 Modifications to ASTM C 227

The examination of lightweight aggregate is not specifically addressed in ASTM C 227. Thus, some alterations to the standard test procedure were necessary for all seven mixes described in Table 1. These changes include allowances in mix proportioning for the significantly lower specific gravity of the HGS, adjustment of the alkali content of the oil well cements, and adjustment of the water-to-cement ratio to allow for flow of this mortar.

2.4 Aggregate Content

ASTM C 227 requires a cement-to-aggregate ratio of 1:2.25 by weight; this ratio implies a normal aggregate specific gravity. Using the ratio specified in ASTM C 227 would require an enormous volume of HGS due to its very low specific gravity (0.46); therefore it was necessary to modify the aggregate content. The most efficient means to account for the density difference between the HGS aggregate and normal weight aggregate is to modify the cement-to-aggregate ratio based on the ratio of specific gravities. This method yields a cement-to-aggregate ratio of 1:0.414.

$$2.25 \times \frac{SG_{HGS}}{SG_{glass}} \qquad \text{Eqn. 1}$$

2.5 Aggregate Gradation

The gradation specified by ASTM C 227 is shown in Table 2. As the HGS are nominally finer than 0.15 mm (No. 100 sieve), they do not conform to this specification. However, ASTM C 227 allows for modifications to the gradation. If the given aggregate is finer than specified, than the mass percent of the first sieve on which the aggregate is retained must be the sum of the mass percentages of the sieves through which it passed. For example, if a given aggregate sample passed both the No. 8 and No. 16 sieve and had some material retained on the No. 30 sieve, the mass percent of the No. 30 sieve would be 60%. The mass percents of the remaining sieves would be unchanged.

According to the Product Information sheet for HGS 6000, less than 1% of the aggregate is retained on the No. 100 sieve, with the remainder of the material finer. Using the modification presented by the standard, 100% of the HGS should be retained on the No. 100 sieve; since this modification is not possible, the HGS was used "as is".

Table 2: Gradation Requirement for ASTM C 227

Sieve No.		Mass
Passing	Retained on	%
4	8	10
8	16	25
16	30	25
30	50	25
50	100	15

2.6 Alkali Content

An equivalent alkali (Na_2O_{eq}) content of at least 0.8% is suggested for ASTM C 227 in ASTM C 33. The alkali content required by ASTM C 227 is 0.6% to test only aggregate reactivity, or the highest available alkali content cement for a specific application. The equivalent alkali content for Mixes 1, 2 and 5 are raised to 1.0% to accelerate the reaction; the alkali content for Mixes 3 and 4 are not increased to simulate actual field conditions. The equivalent alkali content of 1% was chosen based on typical values used previously. Alkali contents used in previous studies have typically ranged from 0.92% (Ducman et al 2002) to 1.0% (Wang and Guillot 1991) when using ASTM C 227, and 1.25% for C 1293 and autoclaving methods (Boyd et al 2002, Fournier et al 1991).

2.7 Water-to-Cement Ratio

The water-to-cement ratio of 1.0 in Mix 5 is based on typical slurry compositions provided by 3M. A w/c of 0.75 with superplasticizers for Mixes 1-4 was determined per ASTM C 227 to obtain a flow of 105%-120%. While typical water-to-cement ratios for concrete fall within the range of 0.35-0.60, unusually high w/c ratios and superplasticizers are used in this study due to the fineness of the HGS, which greatly reduce workability.

2.8 Mixing and Casting Mortar Bars

A 10-L Hobart mixer with speeds of 60, 120, and 180 rpm was used to mix the mortar. The mixer, mixing bowl, and paddle used were in accordance with ASTM C 305, as specified in ASTM C 227. For Mixes 1, 2, and 5, sodium hydroxide was first added to the water and combined with an electric mixer. The amount of sodium hydroxide required to bring the mixes to an equivalent alkali content of 1.0% was determined according to ASTM C 1293.

Flow was tested as outlined in ASTM C 227 and ASTM C 1437 and was required to be between 105%-120%. The mortar was then cast into 1" by 1" by 11.75" brass molds coated with release agent. Mortar was tamped and vibrated to reduce air voids.

After casting the bars, the mortar bars were cured in a moist cure box in over 98% humidity at 23°C for 24±2 hours. Initial length measurements were made for the expansion bars (as detailed in the following section) and stored in a container as required by ASTM C 227. The storage container consists of a sealed metal tank with water in the bottom, absorbent material lining the sides, and inner rings of absorbent material to ensure moisture is provided evenly to all mortar bars. The bars were stored upright and supported by a wire rack and were not in contact with the absorbent material or the water in the bottom of the tank, as detailed in ASTM C 227. The storage container was kept in an oven at 38°C in 100% humidity. Mortar bars to be tested in flexure were cured in a limewater bath. All humidity and temperatures were verified with a hygrometer.

For each mix, two batches were cast on separate days with six mortar bars per batch. From the six bars, two were cast with metal studs to be tested for expansion and the remaining four were cast for flexure tests. After curing in the limewater bath for at least three days, the bars for flexure were cut into thirds, with dimensions of approximately 1"x1"x3.75". Thus, for each of the five mix designs, a total of four expansion bars and six flexure specimens to be tested at four different times were made.

Additional mortar bars were cast for several mixes to assess the effect of curing on the potential for reduced flexural strength due to microcracks caused by alkali-silica reaction. Short-term effects of curing on flexural strength were assessed for Mixes 1 and 2. For these mixes, seven bars were cast per mix. One bar (three specimens) was tested at one day immediately after removal from the mold. For the remaining mortar bars, three were stored in the tank for inducing ASR, and three were placed in the limewater bath. These bars were tested at 7 day and 14 days after demolding to evaluate trends in flexural strength of the two cure methods. Longer-term effects were analyzed for mixes representative of alkali contents in field applications. Two mixes were prepared, one with Class H cement and a water-to-cement of 0.84 (Mix 6), and one with Class A cement and a water-to-cement ratio of 0.81 (Mix 7). Both mixes had no increased alkalinity and an aggregate-to-cement ratio of 0.414. These mixes had mortar stored in both the limewater bath and the ASR-inducing tank, and were tested in flexure at 83 days of exposure.

2.9 Expansion Test

Length measurements for expansion bars were taken with an electronic comparator. A 295 mm reference bar was placed in the comparator and was zeroed. The length difference of the mortar bar was measure to the nearest 0.002 mm. At least three length measurements were made until readings were with 0.004 mm of each other, and the average was recorded as the length difference. The electronic comparator measures positive as downwards. Thus, increasing positive values for the length difference indicates shrinkage. The length of the mortar bars is then determined by subtracting the length difference from the reference bar length of 295 mm.

Initial measurements were taken after demolding, and subsequent measurements were taken at 14, 28, 56, 113, and 172 days of age. Prior to all subsequent expansion testing, the bars were moved from the storage container at 38°C to a similar storage container at 23°C for 16-24 hours to eliminate any expansion from temperature differentiation. After determining the initial length of the mortar bars after one day curing, L_i, and lengths at the appropriate intervals, the amount of expansion or shrinkage was determined as follows:

$$\varepsilon = \frac{L - L_i}{L_i} \times 100\% \qquad \text{Eqn. 2}$$

After testing the mortar bars for expansion, the bars were placed back into the storage container in an inverted position, as required by ASTM C 227, for future measurements.

2.10 Flexure Test

Flexure tests for Mixes 1-5 were performed on the mortar at 14 days, 28 days, 56 days, and 85 days of age, and future testing will include 6-month tests. Flexural testing was performed according to ASTM C 293. After removal from the cure bath, three specimens per batch were allowed to dry for approximately 30 minutes before testing.

For all flexure tests, measurements of depth and width were measured to the nearest 0.001" with an electronic caliper. Before placement in the universal testing machine, all surfaces were ensured to be smooth and free from defects. The specimen was placed in center point bending on a SATEC EMF 22 universal testing machine with a load cell capacity of 22 kips.

The span for each test was 3", measured with an electronic caliper, and the loading rate was set at 0.2 mm/min. An extensometer placed directly under the point load midway along the span was used to measure deflections. For each specimen, the peak load was recorded using the Partner Version 3.0a software. The modulus of rupture (MOR) is determined from Equation 3.6:

$$MOR = \frac{3PL}{2bh^2} \qquad \text{Eqn. 3}$$

where P is the peak load (lb), L is the span length (3"), b is the width (inches), and h is the depth (inches).

2.11 Microscopy

Laser scanning confocal microscopy using the Leica Confocal TCS-NT microscope at 20x magnification and Leica Confocal Software Version 2.00 was used to take images of the fracture surfaces of mortar bars broken in flexure. The image produced is the combination of the maximum projection of a series of 20 images taken over the uneven fracture surface. Leica Stereo Microscope and Image Pro-Plus Version 4.5.1.22 were also used to take images at 80x magnification. These images were examined for signs of reaction product gel around the rims of the HGS and microcracking of the HGS or cement paste. Fracture surfaces remained unpolished so not to induce cracking or to result in loss of any products from ASR.

Microscopy was performed on Mixes 1 and 2 cured under ASTM C 227 conditions at 14 days and cured in the limewater bath at 85 days. Mixes 6 and 7 cured under ASTM C 227 conditions at 83 days were also imaged. Mixes 1 and 2 were chosen for microscopy based on their increased alkalinity and position as the control mixes. Flexure tests were not performed on Mixes 1 and 2 cured under ASTM C 227 longer than 14 days, thus no fracture surfaces were available for microscopy. Mixes 6 and 7 were used for long-term microscopy under ASTM C 227 curing conditions.

3.0 Results and Discussion

3.1 Length Change

3.1.1 Results

Length change results and standard deviations are presented in Figure 1 and Table 3. Expansion data reported is the average of four samples (two from each batch). Data from Mixes 4 and 5 are based on the average of three samples, due to mortars bars breaking during demolding.

Inconsistencies were apparent in length change data with standard deviations as high as 60% of the measured shrinkage (Mix 3, 14 days). However, the majority of the standard deviations were within the range of 10% to 20% of measured shrinkage. And, over time, the variations tended to decrease (i.e., decreasing standard deviations were observed generally with continued exposure). Large standard deviations could indicate that the production of ASR gel was producing randomness in the mortar. However, standard deviation did not appear to increase with time, which, if seen, could signify increased randomness with increasing gel formation. In addition, standard deviation did not significantly increase for mixes with increased alkalinity (Mixes 1, 2, and 5). Figures 2 (a)-(e) show the expansion of individual mortar bars of each mix to evaluate mix and batch consistency. Expansion of mortar bars within the same batch varied very little, as indicated by Figures 2 (a)-(e). The largest inconsistencies in each mix were seen between batches. Mix 1 and 2 had large expansion differences between batches at 28 days with differences of approximately 57% and 36% (Figures 2 (a) and 2(b)), respectively. Mix 3 had significant differences at 14, 56, and 85 days (Figure 2 (c)).

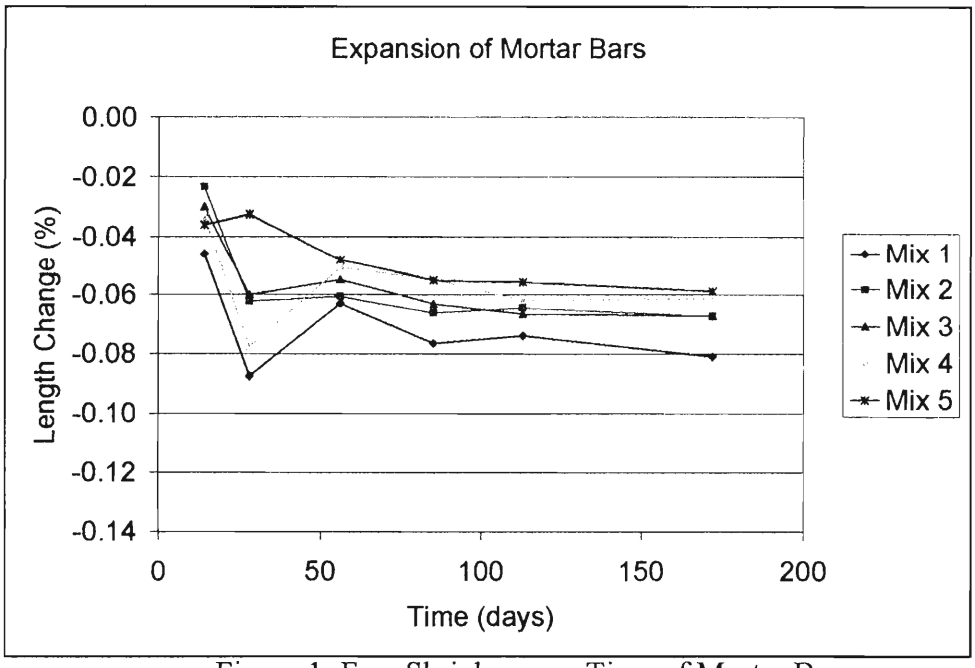

Figure 1: Free Shrinkage vs. Time of Mortar Bars

Table 3: Average Free Shrinkage and (Standard Deviation)

Length Change (%)					
Day	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
14	-0.046 (0.005)	-0.023 (0.002)	-0.029 (0.017)	-0.034 (0.013)	-0.036 (0.008)
28	-0.087 (0.029)	-0.062 (0.033)	-0.060 (0.003)	-0.077 (0.007)	-0.033 (0.003)
56	-0.063 (0.004)	-0.061 (0.001)	-0.064 (0.014)	-0.051 (0.008)	-0.048 (0.006)
85	-0.076 (0.004)	-0.066 (0.003)	-0.072 (0.014)	-0.055 (0.010)	-0.055 (0.006)
113	-0.074 (0.005)	-0.064 (0.003)	-0.075 (0.012)	-0.062 (0.013)	-0.056 (0.006)
172	-0.081 (0.004)	-0.067 (0.002)	-0.067 (0.011)	-0.061 (0.005)	-0.059 (0.004)

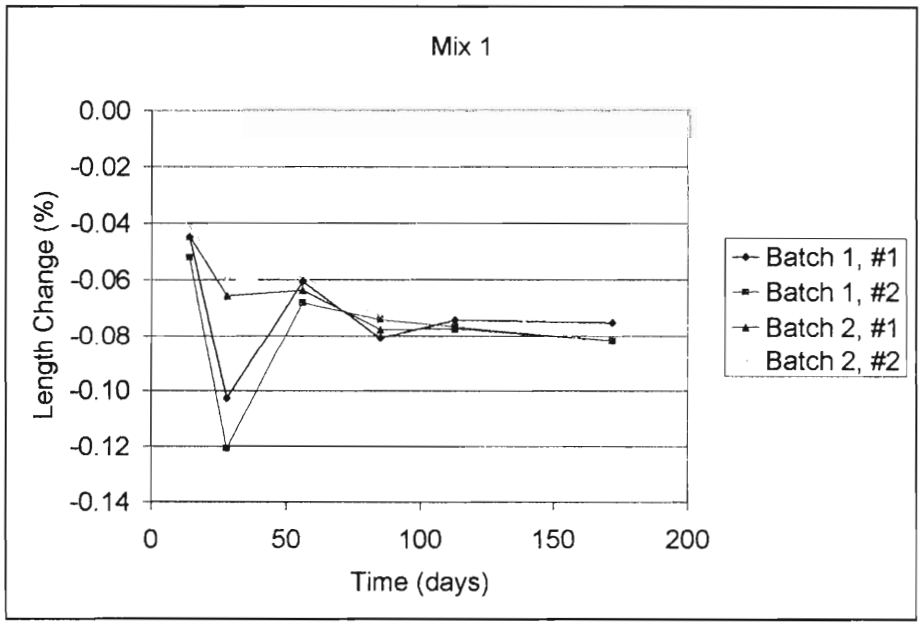

Figure 2 (a): Expansion of Individual Mortar Bars, Mix 1

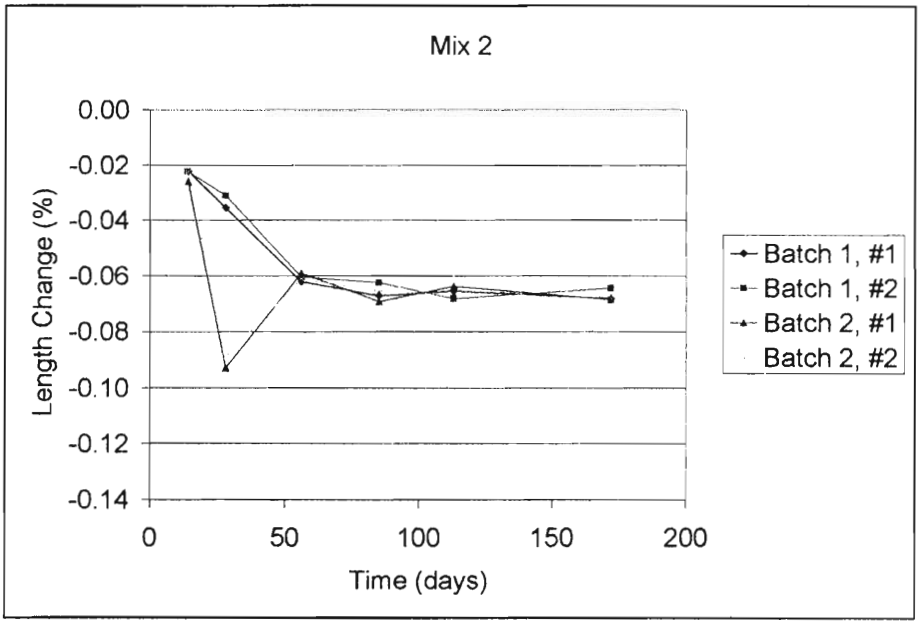

Figure 2 (b): Expansion of Individual Mortar Bars, Mix 2

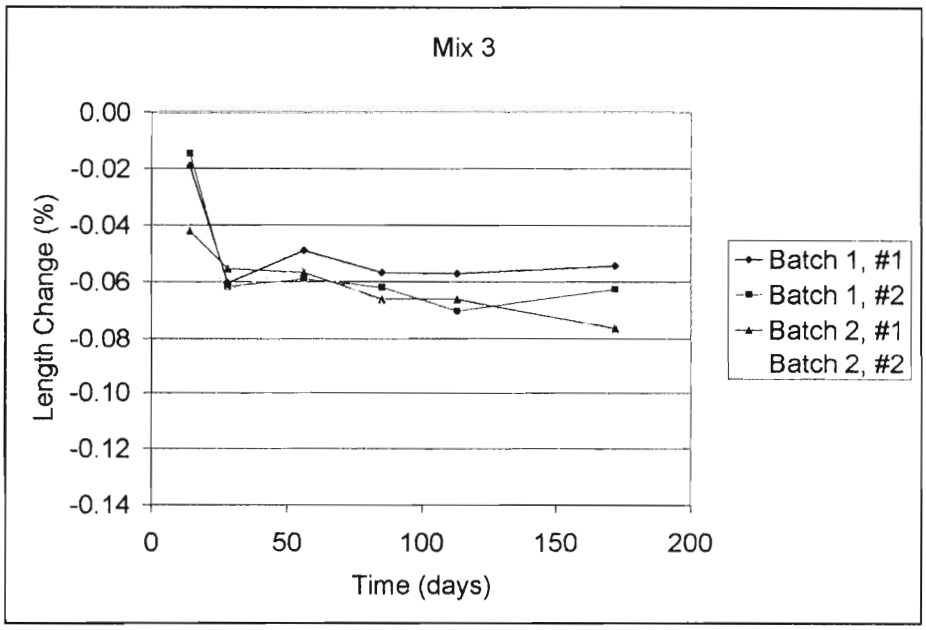

Figure 2 (c): Expansion of Individual Mortar Bars, Mix 3

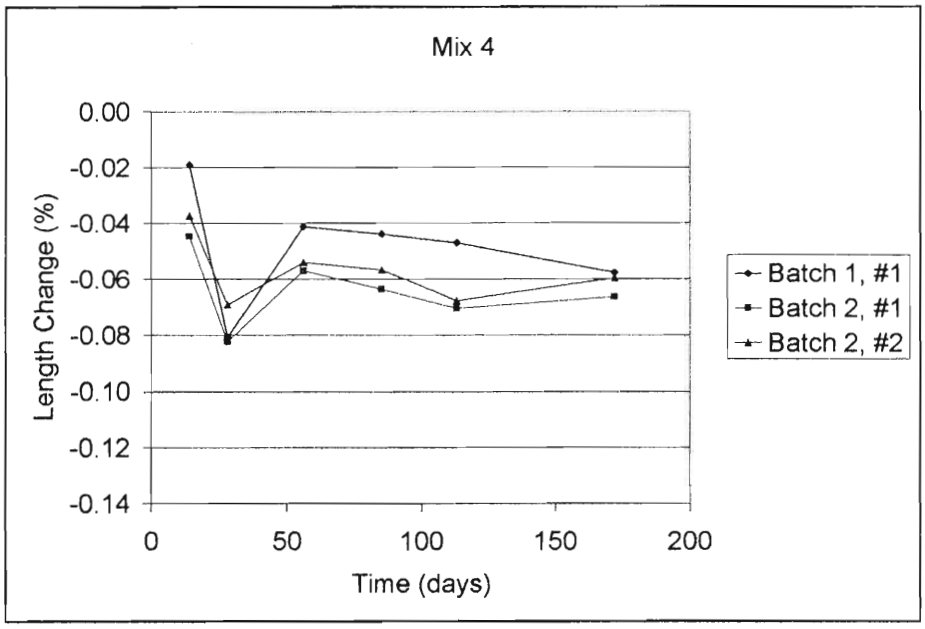

Figure 2 (d): Expansion of Individual Mortar Bars, Mix 4

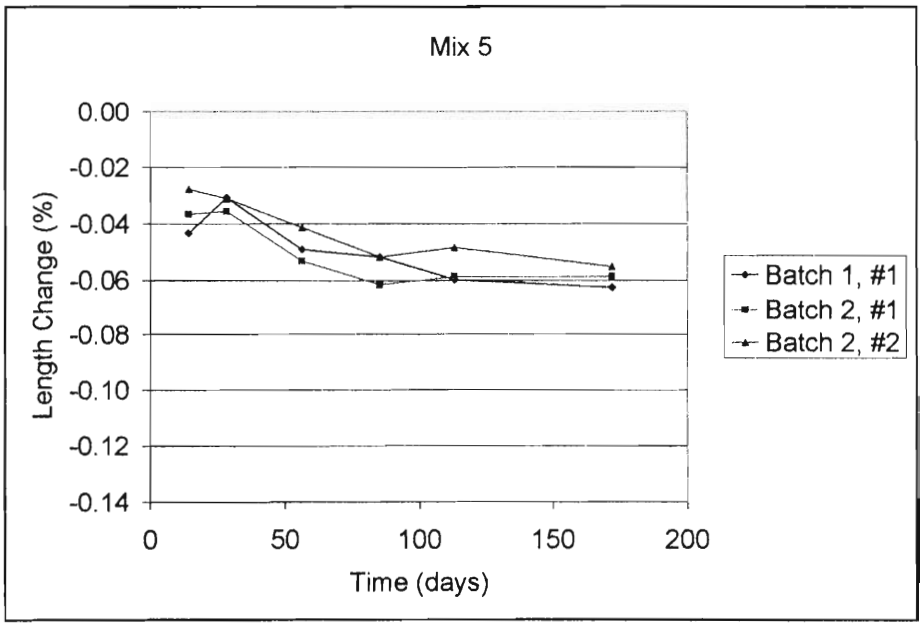

Figure 2 (e): Expansion of Individual Mortar Bars, Mix 5

3.1.2 Discussion

Each of the mixes showed total shrinkage, rather than expansion, over the 172-day examination period. Shrinkage in the bars was unexpected, as the potentially reactive HGS was thought to either cause expansion from ASR or show no significant length change. Shrinkage in these mortar bars is believed to be attributable to autogenous shrinkage and/or carbonation shrinkage.

Autogenous shrinkage is a type of drying shrinkage that occurs during internal hydration in the form of self-dessication (Neville 1997). In autogenous shrinkage, internal moisture losses in capillary pores lead to the formation of menisci which induce a compressive stress on the cement paste. This compressive stress can result in shrinkage. Factors that exacerbate autogenous shrinkage include a low w/c, non-moist curing, high temperatures, and the use of finer materials, such as fine cement or pozzolans (Neville 1997). A w/c greater than 0.42 (Mindness, Young and Darwin 2003) and moist curing promotes hydration and filling of pore space with solid products so that menisci are not formed. Finer materials create a denser cement paste, thus water provided by moist curing is unable to penetrate to the interior.

The use of lightweight aggregate has been shown to affect autogenous shrinkage, depending on the moisture state of the aggregate. Bentur, Igarashi, and Kovler (2001) measured the free autogenous shrinkage of concrete containing normal weight aggregate and concrete with a 25% replacement of the aggregate by volume with lightweight aggregate in the air-dry condition. Autogenous shrinkage was reduced from approximately -0.022% with normal weight aggregate to -0.012% with lightweight aggregate after 7 days. This shrinkage reduction was attributed to the internal supply of water from the aggregate at air dry state. The effect of moisture content and absorption capacity of the aggregate was researched by Kohno et al (1999) who showed that higher initial moisture contents of aggregate result in lower shrinkages due to the internal water supply. Additionally, when oven dry, aggregate with greater absorption capacity will produce more shrinkage due to the increased water absorption (Kohno 1999).

Thus, the high porosity and low moisture content (0.48%) of the HGS most likely contributed to shrinkage observed in the ASTM C 227 test. The effect of very fine lightweight aggregate, such as HGS, on dimensional stability has not been previously addressed in the literature. To examine the potential effect of HGS on autogenous shrinkage, it is necessary to examine the literature discussing autogenous shrinkage in cement-based materials containing silica fume, which like HGS is a finely divided, spherical silicate. Silica fume typically has a composition of 85-98% SiO_2, a mean size of 0.1-0.3 μm, and a surface area of 15-25 m^2/g, whereas HGS is 97% SiO_2, with a larger average particle size of 40 μm and a somewhat smaller surface area of 1.17 m^2/g.

The addition of silica fume has been proven to increase the amount of autogenous shrinkage in cement pastes, mortars, and concrete. Tazawa and Miyazawa (1995) found shrinkage of mortar bars with a w/c of 0.17 and 20% silica fume to have shrinkage values of $800x10^{-6}$ (0.08%) at 28 days. Comparatively, mortar bars cured similarly with w/c of 0.30 and no silica fume had an expansion of $200x10^{-6}$ (0.02%). While this large decrease in expansion is due in part to the lower w/c, the addition of silica fume results in increased autogenous shrinkage. Roy and Larrard (1993) found increasing autogenous shrinkage at 400 days with mortar containing silica fume, but only for w/c less than approximately 0.38. Total shrinkage (autogenous and drying), however, increased with increasing w/c. Mindness, Young, and Darwin (2003) show that a cement paste containing 24% silica fume at a w/(cm) of 0.2 had

autogenous shrinkage of approximately 0.23% at 1000 hours, compared to only 0.08% shrinkage of a paste with no silica fume.

Another potential mechanism leading to shrinkage in these samples is carbonation shrinkage. Carbonation shrinkage results from the reaction of carbon dioxide from the air and the calcium-silicate-hydrate (C-S-H) hydration product. This reaction causes a decrease the in the C/S and water loss (Mindness, Young, and Darwin 2003). Shrinkage occurs due to the subsequent water loss. The carbon dioxide will first react with calcium hydroxide in the cement paste creating calcium carbonate. After depletion of the calcium hydroxide, the C-S-H will react with the carbon dioxide. The reactions are as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad \text{Eqn. 4}$$

$$C\text{-}S\text{-}H + CO_2 \rightarrow C\text{-}S\text{-}H + CaCO_3 + H_2O \quad \text{Eqn. 5}$$

In concrete with pozzolans, the amount of calcium hydroxide is reduced, and therefore less carbon dioxide is needed to complete the reaction. Therefore, the potential for reaction of carbon dioxide with C-S-H is increased with the use of pozzolans (Neville 1997). The use of pozzolans does, however, result in a denser cement paste, which acts to reduce the permeability of the carbon dioxide and lessens carbonation shrinkage. In addition, the relative humidity of the mortar can affect the degree of shrinkage from carbonation. At a low relative humidity, not enough water is present in the pores to transport the carbon dioxide, and at a high relative humidity the pores are saturated and do not permit the transport of carbon dioxide. The rate of carbonation is greatest at a relative humidity of approximately 50% (Mindness, Young, and Darwin 2003).

The high w/c of the mortar bars (0.75 or 1.0) and moist curing condition required by ASTM C 227 would indicate that autogenous shrinkage was unlikely; however, the presence of the HGS increases the likelihood of this reaction. The fineness of the HGS results in a less permeable cement paste, thus water provided during moist curing may be unable to reach the interior. The aggregate was very dry (moisture content of 0.48%), which could further lead to autogenous shrinkage as previously discussed. In addition, if water is able to penetrate the walls of the HGS, further water loss would increase shrinkage. Considering the HGS as a pozzolanic material would enhance the possibility for carbonation shrinkage if a significant portion of the calcium hydroxide is reacted. The high temperature storage conditions may also increase the reaction rates, thus increasing carbonation shrinkage. As with autogenous shrinkage, the dense cement paste and high humidity would decrease carbonation shrinkage. In addition, the use of aggregate can restrain drying and autogenous shrinkage in concrete; no such restraint is provided in the mortar bars.

Theoretical length changes should consider both the potential effects of ASR and shrinkage. Assuming the mixtures are away from the pessimum proportion, the mortar mixes with increased alkalinity (Mixes 1, 2, and 5) should have increased relative expansion. Mixes with finer cement (Type H, Mixes 1, 3, and 5) should have higher shrinkage due to the denser cement paste. The higher w/c of Mix 5 (1.0) may result in less shrinkage, as autogenous shrinkage is reduced with increasing w/c. The effect of decreased shrinkage at increasing w/c is less pronounced at higher w/c, and given the high w/c of Mixes 1-4, increasing the w/c in Mix 5 may not have a significant impact on shrinkage.

Based on the above research, the mortar bars made from Mix 1, 2, and 5 should have the most expansion, or least shrinkage due to increased alkalinity. The effects of cement type and

w/c are expected to be less pronounced than the effects of increased alkalinity. Mix 4 is expected to produce more expansion than Mix 3. The slightly higher alkali content of Type A cement (0.479% compared to 0.325% in Type H) used in Mix 4 would suggest increased expansion over Mix 3 utilizing Type H cement, and the lesser fineness of Type A cement would result in less shrinkage.

Experimental results varied significantly from theoretical. All mortar bars had an initial shrinkage, indicating autogenous shrinkage during hydration. The highest initial shrinkage at 14 days was seen in Mix 1 (w/c of 0.75, increased alkalinity, and Type H cement) at -0.0455%. Due to the increased alkalinity, Mix 1 was expected to have increased expansion over Mixes 3 and 4. Mix 4 (w/c=0.75 and Type A cement) and Mix 5 (w/c=1, increased alkalinity, and Type H cement) had the next highest initial shrinkage at -0.0337% and -0.0360%, respectively. Mix 2 (w/c=0.75, increased alkalinity, and Type A cement) had the least shrinkage at -0.0232%, which agreed with theoretical length change relative to other mixes. Large standard deviations were encountered for Mixes 3 and 4 at 14 days (0.0167 and 0.0132, respectively), as seen in Table 5.

Mixes 1 and 4 showed a large shrinkage between 14 and 28 days, then experienced a significant expansion from 28 to 56 days. These results may indicate an initial autogenous shrinkage followed by expansion, possibly from ASR. This trend could be explained in Mix 1 with increased alkalinity, but is less likely to occur in Mix 4 without increased alkalinity. Furthermore, the mortar bars did not show any significant expansion after this period (28 days to 172 days). The mortar bars in these mixes either continued shrinking or showed only slight expansion.

Mixes 2 and 3 had a large drop in shrinkage value from 14 to 28 days, as was seen in Mixes 1 and 4. These mixes did not, however, display expansion from 28 to 56 days. Rather, shrinkage, or slight expansion, was seen to the end of the testing period. Mix 5 displayed expansion from 14 to 28 days, and then had continued shrinkage to the end of testing. The larger w/c of Mix 5 may have reduced the shrinkage, thus allowing for expansion from 28 to 56 days, however, the continued shrinkage does not support this theory.

At the end of testing, Mix 5 had the least shrinkage possibly due to the increased w/c, which would reduce autogenous shrinkage, and the increased alkalinity, which would exacerbate ASR. Mixes cast with Class A cement (Mixes 2 and 4) had less shrinkage then mixes with Class H (Mixes 1 and 3), which supports theoretical results. The effect of increasing the equivalent alkali content was unexpected. Larger expansion (or decreased shrinkage) is expected if ASR is occurring. This variable did not, however, have a significant impact on expansion.

Reasons for less expansion than expected may be due to leaching of the alkalis or the presence of air voids. Leaching is a common problem with ASTM C 227. If leaching did occur, the reduction of alkalis in the mortar would reduce the rate of ASR. In addition, the presence of air voids would allow the gel a space to migrate, therefore not resulting in expansion. Although the mortar bars were both tamped and vibrated, the presence of air voids was encountered by examining the fracture surface of the samples tested in flexure. Also, the interior of the HGS, if the surface has been damaged, may allow for accumulation of ASR product without expansion of the sample. No evidence of these scenarios, however, was observed during the microscopy performed to date (Section 3.3).

3.2 Flexure Strength

3.2.1 Results

The modulus of rupture as a function of time and standard deviations for the Mixes 1-5 stored in the limewater bath is presented in Figure 3 and Table 4. For each mix, six specimens were tested (three from each batch) at each age. Some bars were broken during demolding, consequently not all mixes at each date were based on six tests. Figures 4 and 5 depict the effect of curing on the alkali-silica reactivity of the HGS for Mixes 1 and 2 up to 14 days and Mixes 6 and 7 at 85 days, respectively.

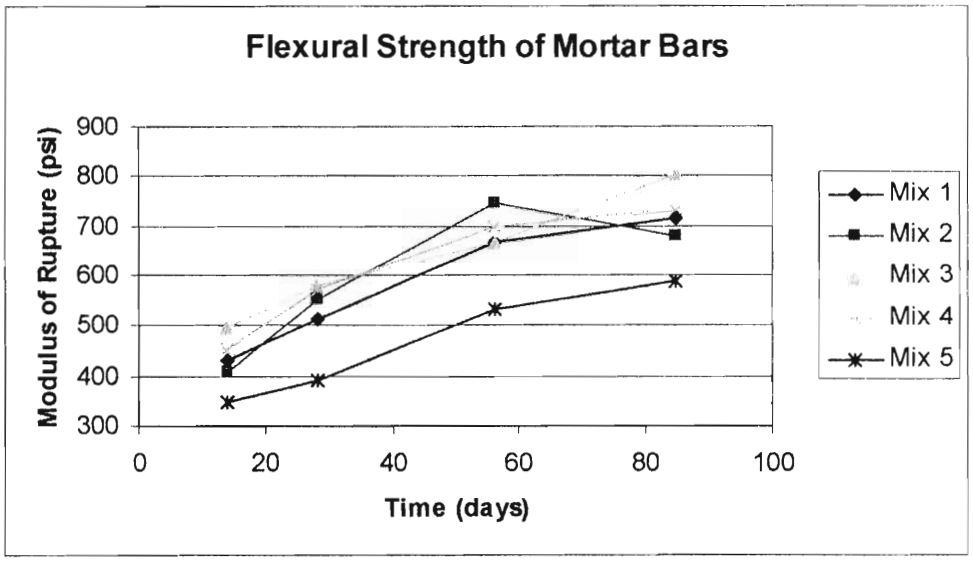

Figure 3: Modulus of Rupture for Mortar Bars Cured in Limewater Bath

Table 4: Modulus of Rupture Data, Mixes 1-5 Limewater Bath

	Modulus of Rupture (psi)					
	Day	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
Average	14	430	406	495	452	348
St Dev		99	70	69	61	148
Average	28	512	554	579	573	392
St Dev		77	160	62	71	46
Average	56	666	746	667	701	534
St Dev		174	104	144	161	62
Average	85	713	681	807	735	588
St Dev		83	145	82	111	100

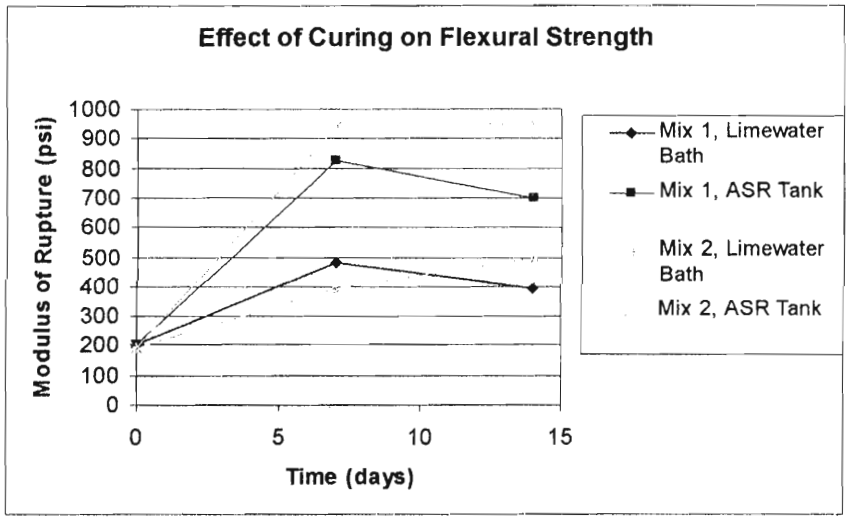

Figure 4: Comparison of Modulus of Rupture for Limewater Bath Curing and ASR Tank Curing up to 14 days of exposure

Table 5: Standard Deviations of Modulus of Rupture Data, Mixes 1and 2 Limewater Bath and ASR Tank

Modulus of Rupture (psi)					
		Mix 1		Mix 2	
Day		Cure Bath	ASR Tank	Cure Bath	ASR Tank
0	Avg	202		190	
	St Dev	22		20	
7	Avg	481	824	394	939
	St Dev	70	82	38	128
14	Avg	392	699	497	952
	St Dev	44	80	23	72

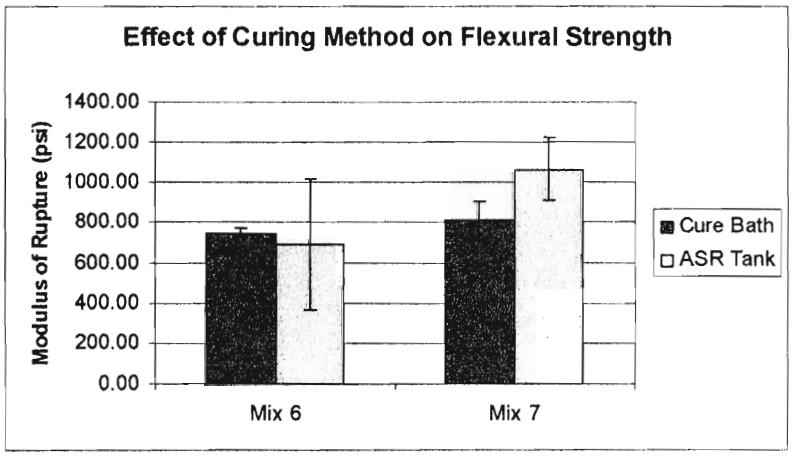

Figure 5: Comparison of Modulus of Rupture for Limewater Bath Curing and ASR Tank Curing at 83 days of age

3.2.2 Discussion

Flexure capacity of concrete or mortar is very sensitive to microcracking, thus the presence of ASR can decrease flexural strength due to microcracking from expansion. Figure 3 shows increasing flexural strength with increasing time, indicating that ASR may not be occurring. A reduction in flexural strength was seen in Mix 2 from 56 to 85 days. The standard deviation was approximately 20% of the average, indicating that this reduction in flexural strength may or may not be significant.

The effect of curing type on flexural strength produced conflicting results with expected trends. Mortar bars cured under ASTM C 227 are expected to have increased alkali-silica reactivity from the elevated temperature, thus increasing the potential for microcracking and reduced flexural strength. Figure 4 comparing the flexural strength of Mixes 1 and 2 under ASTM C 227 curing (ASR tank) and limewater bath curing show higher values of modulus of rupture for mortar bars cured under ASTM C 227. A decrease was seen for Mix 1 under both curing conditions from 7 to 14 days, indicating possible microcracking from ASR. The standard deviations were relatively small, within the range of 5% to 15% of the average modulus of rupture. Longer term effects (85 days) of mixes without increased alkalinity, as is relevant to field applications, are seen in Figure 5. Mortar bars cured under ASTM C 227 have a lower modulus of rupture for Mix 6; the opposite trend is observed in Mix 7. Standard deviations were larger for mortar bars cured under ASTM C 227.

High standard deviations in flexural strength may be attributed to the randomness of the microcracking. In center point bending, flexure cracks theoretically originate in the center, where the moment is greatest, and on the bottom face. The position of potentially already present microcracks formed from expansion due to ASR will affect the degree of detrimental effects on modulus of rupture. Microcracks centered near the midspan at the bottom face will reduce the modulus of rupture; those near the top face and away from the center will have little or no effect of the modulus of rupture. From this principle, mortar bars with identical properties (dimensions and composition) could show significant variations in flexural strength.

Another mechanism by which large standard deviations could be present is due to overloading of the mortar bars during test set up. The testing machine crosshead is lowered manually until the round bar applying the point load to the specimen is barely touching and just stays in place. Due to the weak nature of the mortar bars from high w/c, accidental overloading of the specimen during this step can induce cracking, thus producing reduced flexural capacity results. Additionally, large standard deviations are present due to the reduced number of test specimens. The mortar samples tested at 0 and 7 days of exposure with compositions matching those of Mixes 1 and 2 for each curing condition and those for Mixes 6 and 7 consisted of three samples.

Assessing the presence and extent of damage from ASR utilizing flexural strength is difficult. Lower strengths may indicate microcracking caused by ASR; however, due to the randomness of microcracking, large standard deviations are common. Additionally, air voids, much like microcracking, can also lower the modulus of rupture. Flexure testing can provide useful information for gauging damage in mortar from ASR in conjunction with expansion tests; however, tension or compression tests may provide results with less deviation.

3.3 Microscopy

Fracture surfaces of the mortar bars were examined to look for microcracking or the presence of ASR-product gel. The Leica TCS NT confocal microscope and Leica Version 1.0 software was used to take images of fracture surfaces of mortar bars broken in flexure for Mixes 1 and 2 at 14 days of exposure in the ASR tank, Mixes 1 and 2 at 85 days cured in limewater bath, and Mixes 6 and 7 at 83 days cured in ASR tank. A Leica Stereo Microscope was also used to take images. These images are shown in Figures 6 (a)-(l).

No microcracking was visible; however, Figure 6 (k) shows a thin film of white surrounding the HGS. This layer is believed to be either ASR reaction product gel or delamination of the HGS from the paste.

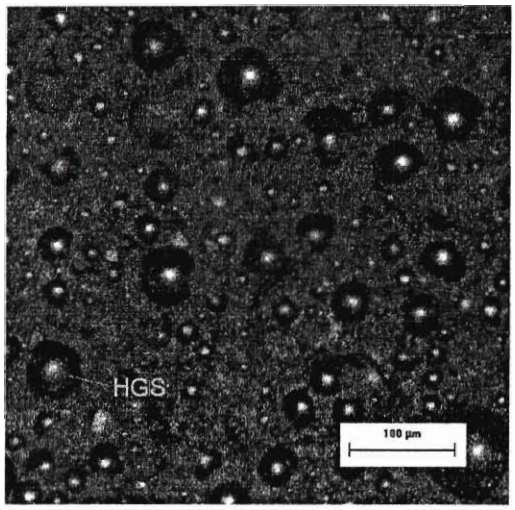

Figure 6 (a): Mix 1, 14 days, ASR tank Confocal Microscope

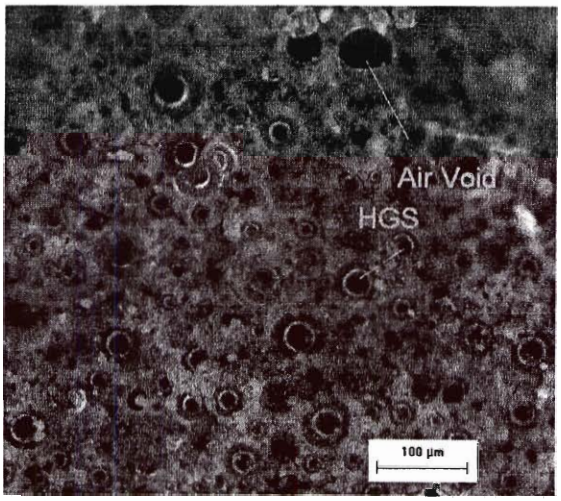

Figure 6 (b): Mix 1, 14 days, ASR tank Stereo Microscope

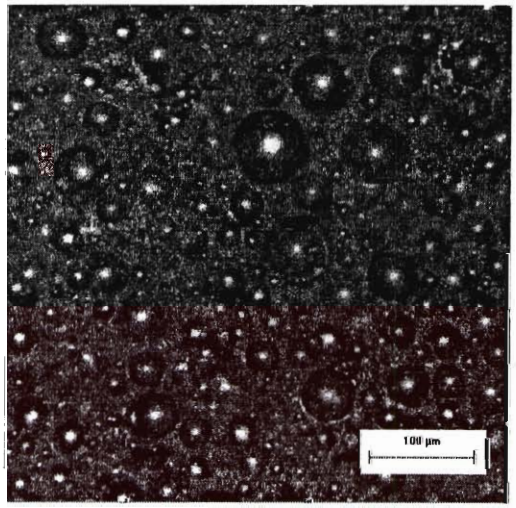

Figure 6 (c): Mix 2, 14 days, ASR tank Confocal Microscope

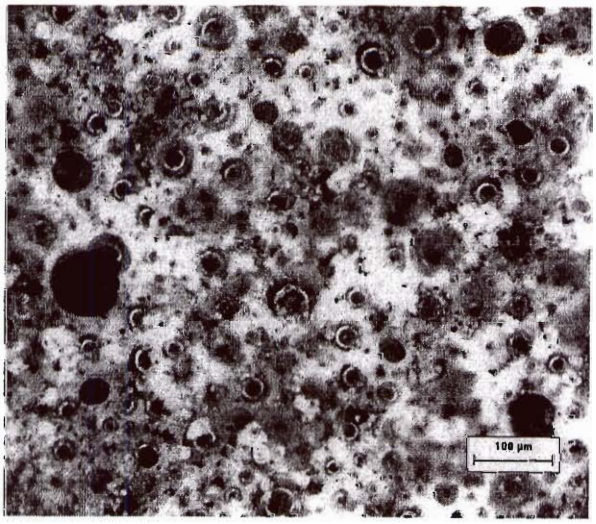

Figure 6 (d): Mix 2, 14 days, ASR tank, Stereo Microscope

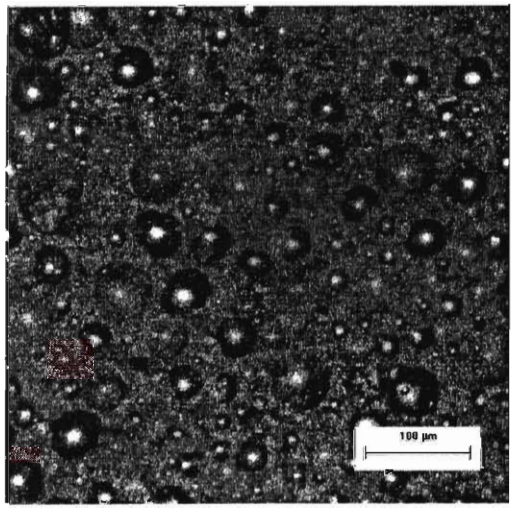

Figure 6 (e): Mix 1, 85 days,
Limewater bath, Confocal Microscope

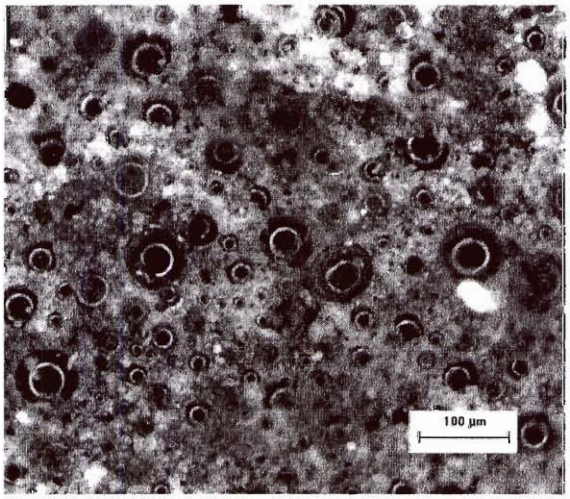

Figure 6 (f): Mix 1, 85 days,
Limewater bath, Stereo Microscope

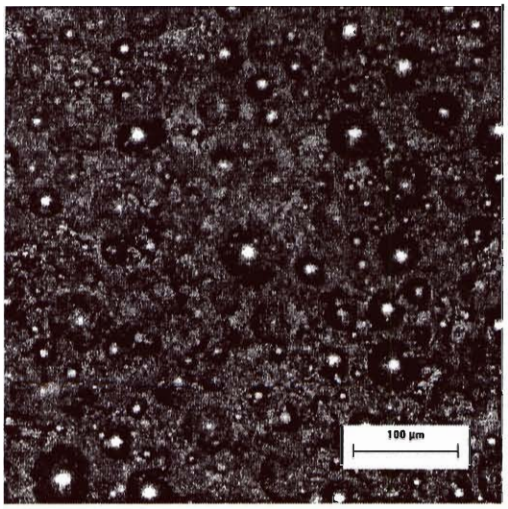

Figure 6 (g): Mix 2, 85 days,
Limewater bath, Confocal Microscope

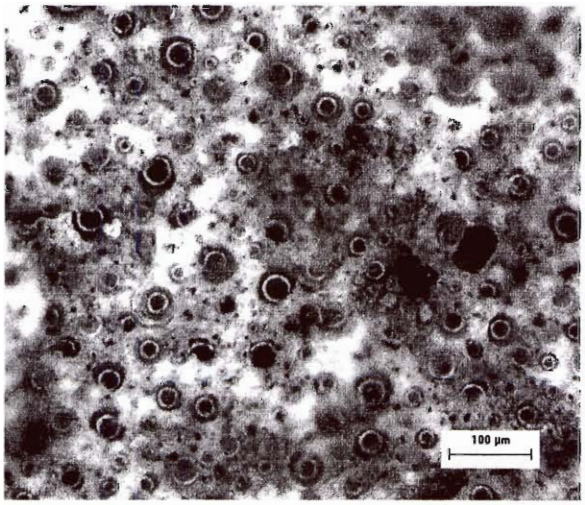

Figure 6 (h): Mix 2, 85 days,
Limewater bath, Stereo Microscope

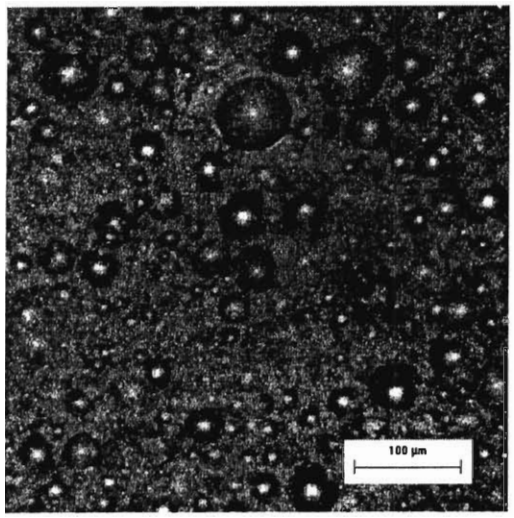

Figure 6 (i): Mix 6, 83 days, ASR tank Confocal Microscope

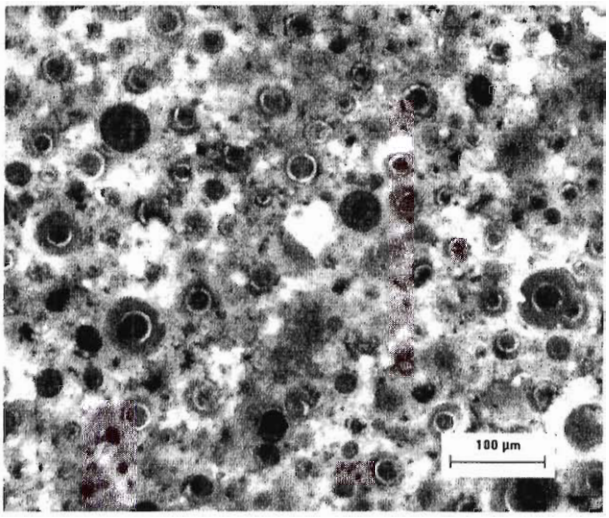

Figure 6 (j): Mix 6, 83 days, ASR tank Stereo Microscope

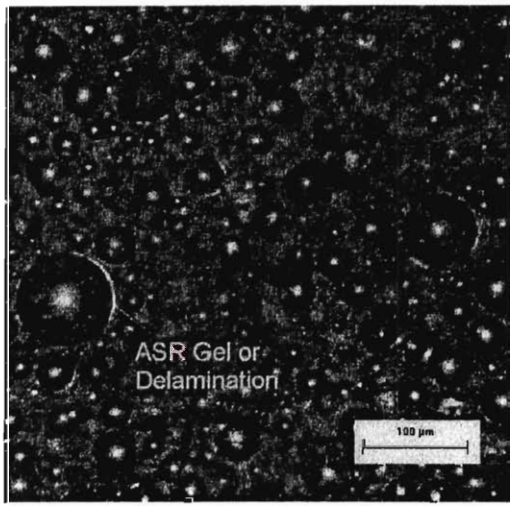

Figure 6 (k): Mix 7, 83 days, ASR tank Confocal Microscope

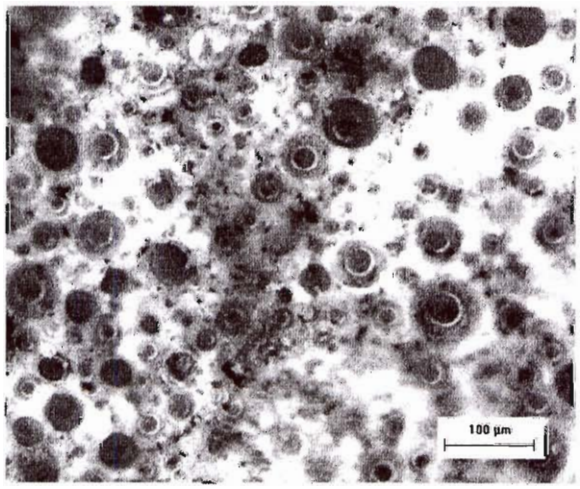

Figure 6 (l): Mix 7, 83 days, ASR tank Stereo Microscope

4.0 Conclusions and Recommendations

From the given data of expansion, flexural strength, and microscopy, alkali-silica reaction does not seem to be occurring under these testing conditions. ASTM C 227 can, however, be unconservative. Continued long term testing of expansion using ASTM C 227 of one year is suggested to better gauge the reactivity of the HGS. Future testing with ASTM C 227 and microscopy will determine whether the aggregate is reactive under the testing conditions (38°C).

Since ASTM C 1260 has previously shown the HGS to be reactive, Phase II testing should include another method of testing in addition to continued ASTM C 227 testing. Despite the shortcomings of ASTM C 1293 previously discussed, this test is widely accepted and best indicates field performance of aggregate. Modifications to the aggregate content of this test will be needed since both coarse and fine aggregate are required. In addition, the low w/c required by this test (0.42-0.45) is expected to produce a mortar that is unworkable. It is suggested that the *HGS be tested in both mortar mixes representing typical design mixes and concrete meeting* ASTM C 1293 standards.

Neither ASTM C 1293, 1260, nor 227 simulate the elevated temperature and pressure conditions encountered in oil well cementing. These increased temperatures and pressures will most likely encourage ASR. Thus, it is suggested that an autoclaving technique with temperatures and pressures consistent with oil well applications be used to measure expansion. The autoclaving method used to test for ASR at high temperatures and pressures best simulates the conditions of oil well cementing. However, the ASTM standard C 151 for autoclaving is not directly stated to be used as a test for ASR. A simple solution would be to combine this test with the batching specifications of ASTM C 227, with the addition of expansion limits derived from testing. Currently there are no accepted limits for expansion under these conditions. Thus, the limits for expansion would have to be the subject of considerable prior testing and comparison to field performance.

Flexure testing resulted in large standard deviations, thus the effect of ASR was difficult to establish. Either compression or tensile strength testing is suggested.

Finally, because ASTM C227 test results showed shrinkage, rather than expansion, it is recommended that autogenous shrinkage testing be performed on slurries typically used for oil well cementing applications.

References

3M Product Information Sheet, Hollow Glass Spheres 6000, www.3M.com, 2002.

Ahmed, T., E. Burley, and S. Rigden. "The Effect of Alkali-Silica Reation on the Fatigue Behavior of Plain Concrete Tested in Compression, Indirect Tension, and Flexure." *Magazine of Concrete Research*, Vol. 51 No. 6, pgs 375-390, 1999.

Arco, Manny. Personal communications, 2002.

Bensted, J. "Class G and H Basic Oilwell Cements." *World Cement*, Vol. 23 No. 4, pgs 44-48, 1992.

Bentur, A., S. Igarashi, and K. Kovler. "Prevention of Autogenous Shrinkage in High-Strength Concrete by Internal Curing using Wet Lightweight Aggregates." *Cement and Concrete Research*, Vol. 31 No. 11, pgs 1587-1591, 2001.

Boyd, S., T. Brenner, and T. Holm. "Addition of Lightweight Aggregate Reduces Expansion in Concrete Containing Highly Reactive Normal Weight Aggregate." *Proceedings of the 11th International Conference of Alkali-Aggregate Reaction in Concrete*, ed. M. A. Berube, B. Fournier, and B. Durand, pgs 593-602, 2000.

Chapuis, R. P. and P. P. Legare. "A Simple Method for Determining the Surface Area of Fine Aggregate and Fillers in Bituminous Mixtures." *ASTM Special Technical Publication*, No. 1147, ASTM, pgs 177-186, 1992.

Ducman, V., A. Mladenovic, and J. S. Suput. "Lightweight Aggregate based on Waste Glass and its Alkali-Silica Reactivity." *Cement and Concrete Research*, Vol. 32, pgs 223-226, 2002.

Fournier, B., M. A. Berube, and G. Bergeron. "A Rapid Autoclave Mortar Bar Method to Determine the Potential Alkali-Silica Reactivity of St. Lawerence Lowlands Carbonate Aggregates (Quebec, Canada)." *Cement, Concrete, and Aggregates*, CCAGDP, Vol. 13 No. 1, pgs 58-71, 1991.

Hudec, P. and R. C. Ghamari. "Ground Waste Glass as an Alkali-Silica Reactivity Inhibitor." *Proceedings of the 11th International Conference of Alkali-Silica Reaction in Concrete*, ed. M. A. Berube, B. Fournier, and B. Durand, pgs 663-672, 2000.

Jin, W., C. Meyer, and S. Baxter. "Glascrete – Concrete with Glass Aggregate." *ACI Materials Journal*, Vol. 97 No. 2, pgs 203-213, 2000.

Kohno, K., T. Okamoto, Y Isikawa, T. Sibata, and H. Mori. "Effects of Artificial Lightweight Aggregate on Autogenous Shrinkage of Concrete." *Cement and Concrete Research*, Vol. 29 No. 4, pgs 611-614, 1999.

Mindness, S., J. F. Young, and D. Darwin. Concrete, 2nd edition, Prentice Hall, 2003.

Monette, L., N. Gardner, and P. Grattan-Bellew. "Residual Strength of Reinforced Concrete Beams Damaged by Alkali-Silica Reaction –Examination of Damage Rating Index Method." *ACI Materials Journal*, Vol. 99 No. 1, pgs 42-50, 2002.

Neville, A. M. Properties of Concrete, 4th edition. John Wiley and Sons, 1998.

Roberts, F., P. S. Kandhal, E. R. Brown, D. Lee, and T. Kennedy. Hot Mix Asphalt Materials, Mixture Design, and Construction, 2nd edition, NAPA Research and Education Foundation, 1991.

Roy, R. and F. de Larrard. "Creep and Shrinkage of High-Performance Concrete: The LCPC Experience." *Proceedings of the Fifth International RILEM Symposium in Barcelona*. E&FN Spon, London, pgs 500-508, 1993.

Smith, R. Well Cementing, Preface. Erik B. Nelson, Editor. Elsevier Science Publishers, 1990.

Tang, M. S., S. H. Zhen, and S. F. Han. "A Rapid Method for Identification of Alkali Reactivity of Aggregate." *Cement and Concrete Research*, Vol. 13 No. 3, pgs 417-422, 1983.

Tazawa, E. and S. Miyazawa. "Experimental Study on Mechanism of Autogenous Shrinkage of Concrete." *Cement and Concrete Research*, Vol. 25 No. 8, pgs 1633-1638.

Wang, H. and J. E. Guillott. "Mechanisms of Alkali-Silica Reaction and the Significance of Calcium Hydroxide." *Cement and Concrete Research*, Vol. 21, pgs 647-654, 1991.